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# The Coefficients of Thermal Expansion of Boron Arsenide ( $B_{12}As_2$ ) Between 25°C and 850°C

C.E. Whiteley<sup>1</sup>, M.J. Kirkham<sup>2</sup>, and J.H. Edgar<sup>1</sup>

<sup>1</sup> *Department of Chemical Engineering, Kansas State University, Manhattan KS 66506*

<sup>2</sup> *High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge TN 37831*

## ABSTRACT

The present investigation was undertaken to determine the coefficients of thermal expansion for the boron-rich compound semiconductor icosahedral boron arsenide ( $B_{12}As_2$ ).  $B_{12}As_2$  powder was synthesized in a sealed quartz ampoule containing boron and arsenic heated to 1100°C and 600 °C respectively for 72 hours. The lattice constants of the  $B_{12}As_2$  were measured by high temperature X-ray diffraction (HTXRD) between 25°C and 850°C. The average lattice coefficients of thermal expansion were calculated perpendicular and parallel to the  $\langle 111 \rangle$  axis in the rhombohedral setting (equivalent to the  $a$  and  $c$  axes in the hexagonal setting) as  $4.9 \times 10^{-6} \text{ K}^{-1}$  and  $5.3 \times 10^{-6} \text{ K}^{-1}$ , respectively. The average unit cell volumetric coefficient of thermal expansion was  $15.0 \times 10^{-6} \text{ K}^{-1}$ . Knowing these values can be useful in explaining the cracking that occurs in heteroepitaxial  $B_{12}As_2$  thin films and crystals precipitated from metal solutions upon cooling from their synthesis temperatures.

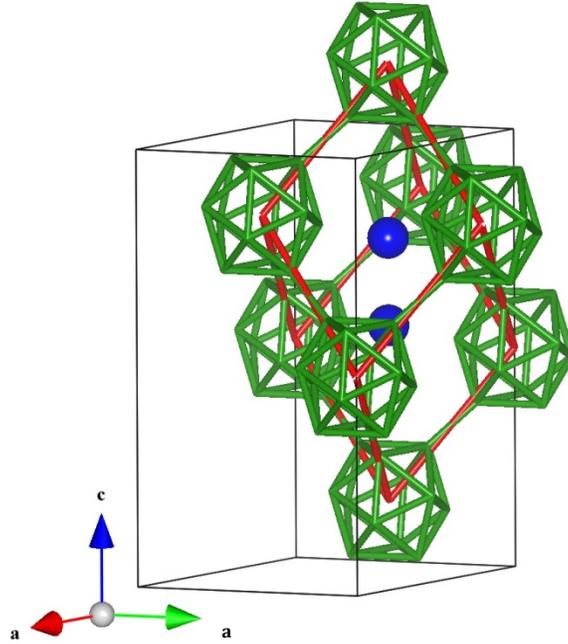
## I. INTRODUCTION

Boron compound semiconductors have unique properties that make them good candidates for a variety of applications including thermoelectrics, neutron detectors, and direct nuclear to electric power conversion. Unlike well-established wide band gap semiconductors like as GaN or SiC, in general boron compound semiconductors have rarely been studied; many of their fundamental properties have not been measured. This is especially true of the icosahedral-structure boron-rich compounds, including  $\alpha$ -boron,  $B_{12}P_2$ ,  $B_{12}As_2$ , and  $B_{12+x}C_{3-x}$ , where two or three-atom chains, As-As or B-C-B for example, lie along the  $\langle 111 \rangle$  axis of the rhombohedral unit cell, (equivalent to the  $c$ -axis of the hexagonal unit cell) [1,2,3]. Icosahedral borides contain 12- boron atom clusters where the boron atoms reside on the vertices of icosahedra, as shown in Figure 1. The icosahedral borides hold a unique position within chemistry because their internal bonding is electron-deficient; two electrons are shared among three boron atoms. The excellent strength of the these three-center bonds imparts the icosahedral borides with extraordinary hardness,  $>200 \text{ GPa}$  [4], and high melting temperatures,  $>2000^\circ\text{C}$  [1,2,3,4].

One previously unreported property for icosahedral boron arsenide is its thermal expansion behavior. Knowing the coefficients of thermal expansion (CTE) for  $B_{12}As_2$  is important for understanding its properties when produced by both the solution growth method [5] and as thin films deposited by chemical vapor deposition (CVD) [6-7]. The  $B_{12}As_2$  can be strained on cooling from its synthesis temperature. Nagarajan *et al* [6] observed that  $B_{12}As_2$  films were cracked on 6H-SiC substrates, presumably due to the differences in the CTE of  $B_{12}As_2$  and the substrate. The crack density increased with film

thickness; ultimately they delaminated from the substrate, for  $B_{12}As_2$  films as thin as 4 - 5  $\mu\text{m}$  [2].

The coefficient of thermal expansion (CTE) describes the lattice expansion with temperature [8]. The properties of icosahedral boride are anisotropic, thus complete characterization of its thermal expansion behavior requires measurements in multiple crystallographic directions. From the lattice CTE values, the lattice volumetric expansion can be calculated.



**Figure 1 - Rhombohedral unit cell of  $B_{12}As_2$ , shown in red, with icosahedral boron clusters (in green) at the vertices and As-As (in blue) chains along the body diagonal, the rhombohedral [111] direction, and also showing the relationship to the axes and unit cell (in black) of the hexagonal setting.**

The volumetric and linear coefficients of thermal expansion are given, respectively, by equations 1 and 2 [8,9].

$$\alpha_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (1)$$

$$\alpha_L = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p \quad (2)$$

Where  $V$  is the specific volume,  $T$  is the temperature, and  $L$  is a characteristic length. If the expansion coefficients do not change much over the temperature range, the equations can be estimated by equations 3 and 4 [8,9].

$$\alpha_v = \frac{1}{V} \left( \frac{\Delta V}{\Delta T} \right) \quad (3)$$

$$\alpha_L = \frac{1}{L} \left( \frac{\Delta L}{\Delta T} \right) \quad (4)$$

By using X-ray diffraction (XRD), the lattice constants can be measured over a temperature range, and the thermal expansion can be directly calculated. The thermal expansion in the two main directions, parallel to the  $a$  and  $c$  axes of the hexagonal unit cell, are calculated from equations 5 and 6 [10], where  $a$  and  $c$  are the lattice constants.

$$\alpha_a(T) = \frac{a - a_{293}}{a_{293}(T - 293)} \quad (5)$$

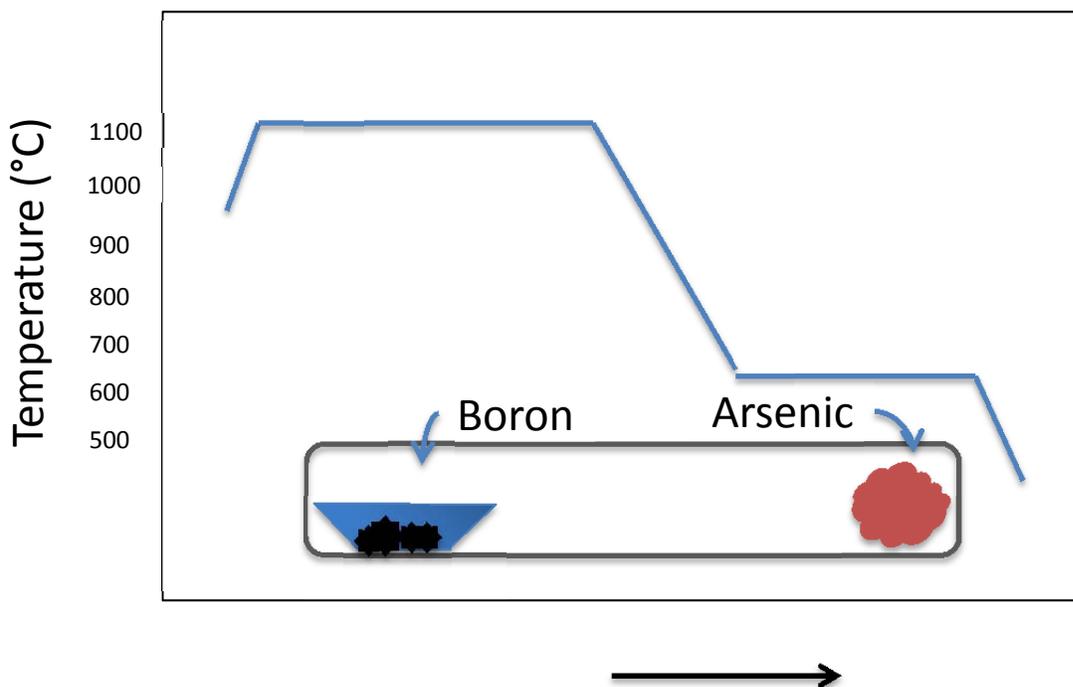
$$\alpha_c(T) = \frac{c - c_{293}}{c_{293}(T - 293)} \quad (6)$$

Note that 293 K is used by convention as the reference temperature for thermal expansion coefficients. Tsagareishvili *et al* [10], Rice [11] and Yakel [12] completed thorough investigations of the coefficient of thermal expansion of boron carbide, reporting an average CTE for the  $a$  direction of  $5.73 \times 10^{-6} \text{ K}^{-1}$  (25-940°C),  $5.29 \times 10^{-6} \text{ K}^{-1}$  (25-600°C) and for the  $c$  direction of  $5.65 \times 10^{-6} \text{ K}^{-1}$  (25-940°C), and  $6.25 \times 10^{-6} \text{ K}^{-1}$  (25-600°C) [11]. Anisotropy in boron carbide of up to 15% can be explained by the differences in the  $a$  and  $c$  directions of the hexagonal structure [10-12]. The strong covalent bonds of the icosahedra should show less flexibility than the bonds between the carbon atoms parallel to the  $c$  axis.

Boron carbide and boron arsenide have the same space group (R-3m) and similar boron-to-boron bonds between boron icosahedra, thus it is expected that the coefficients of thermal expansion should also be comparable, and anisotropic. For that reason, the coefficients of thermal expansion of  $\text{B}_{12}\text{As}_2$  powder were measured by HTXRD between 25 and 850°C.

## II. EXPERIMENTAL METHODS

$\text{B}_{12}\text{As}_2$  powder was synthesized by a method similar to that described by Ku [13]. The fine powder boron (99.999%) and arsenic (99.999%) source materials were first weighed (150g each) and placed in an unsealed quartz ampoule, separated by 15 cm. The tube was then evacuated to  $10^{-6}$  torr, and while still under vacuum, heated to 125°C for 5h to remove any residual contaminants (such as water) that were absorbed on the surfaces of the powders. After the baking cycle, the ampoule was sealed and inserted into a horizontal resistance heater, as shown in Figure 2. The boron was maintained at 1100°C, and the arsenic was held at 600°C (creating an As vapor pressure of approximately 0.5 atm) [14]. After 72h the ampoule was cooled to room temperature and opened to recover the powder. XRD measurements were then taken to confirm the phase purity of icosahedral boron arsenide, and to test whether impurities were present, as would be indicated by additional peaks.



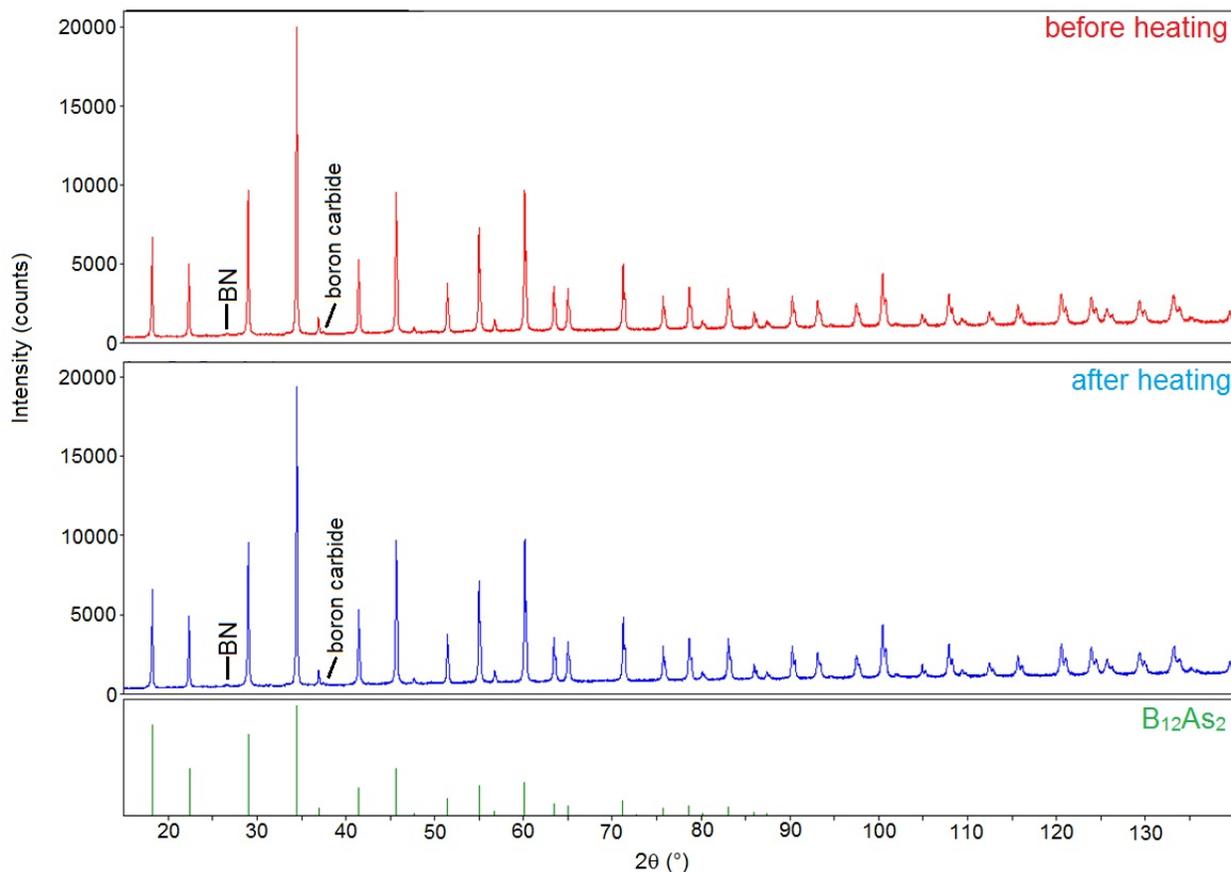
**Figure 2 – Schematic of the temperature profile in the furnace during the synthesis of  $B_{12}As_2$  powder. Note that the boron is held in the hot zone and the arsenic is held in a cooler zone (to maintain 0.5atm).**

In order to monitor the crystal structure of  $B_{12}As_2$ , high temperature X-ray diffraction measurements were carried out on both heating and cooling between 25°C and 850°C in 1 atm of  $N_2$ . A PANalytical X'Pert Pro MPD X-ray diffractometer with automatic divergence slits and a position sensitive detector was employed to record the diffraction data in the  $2\theta$  range 10–140° with a step of 0.0167°. The X-ray source was Cu-K $\alpha$  with a wavelength of 1.54060 Å. The accelerating voltage was 45 kV and the current was 40 mA. The samples were heated in an Anton Paar XRK 900 reaction chamber under flowing  $N_2$ . The heating rate was 25°C min<sup>-1</sup> between data collection steps at 25°C, every 100° between 100 and 800°C, and at 850°C. After the measurements were taken, the data were analyzed with JADE v.3.5 software [MDI, Livermore, CA], and the spectra were analyzed to determine the changes in lattice parameter as a function of temperature. The precision of the lattice parameters was 0.0002Å and the temperature error was  $\pm 2^\circ C$ .

### III. RESULTS AND DISCUSSION

The synthesis of  $B_{12}As_2$  is easily accomplished in sealed quartz ampoules at 1100°C and 0.5atm. XRD analysis at room temperature revealed the product was high purity icosahedral boron arsenide. The diffraction peaks match those expected for the  $B_{12}As_2$  structure (Inorganic Crystal Structure Database #68151), as shown in Figure 3. The room temperature (298K) lattice constants for  $B_{12}As_2$  were  $a = 6.1417 \text{ \AA}$  and  $c = 11.9093 \text{ \AA}$  in close agreement with previously reported values [15-16]. There also small intensity hBN

and  $B_4C$  peaks, presumably from reactions with the boats and containers of the original boron.



**Figure 3 - Room temperature XRD diffractogram for  $B_{12}As_2$  powder before (top) and after (bottom) heating to 850°C. All peaks were identified to be associated with boron arsenide, by comparison with the  $B_{12}As_2$  reference pattern at the bottom. Trace impurity peaks were observed, which could correspond to the strongest peaks of boron carbide (37.5° 2theta) and boron nitride (26.7° 2theta).**

While examining the  $B_{12}As_2$  powder at high temperature, no fundamental changes in the diffractogram took place. Had decomposition occurred, it could have been detected by the appearance, and increase in intensity, of new peaks as the temperature approached 850°C; however, no new peaks were observed. The XRD spectra after heating exhibited no changes from, as shown in Figure 3.

The lattice parameters of the  $B_{12}As_2$  powder increased with temperature between 25°C and 850°C, fitting closely to quadratic curves ( $R^2 = 0.9999$ ). The volumetric and linear coefficients of thermal expansion (CTEs) were calculated from the lattice parameters, as in equations (5) and (6). The CTEs are plotted as a function of temperature in Figure 4. Their relationships with temperature were fitted using a least-squares regression to the equation

$$\alpha (K^{-1}) = \alpha_0 + \alpha_1 T + \alpha_2 / T^2 \quad (7)$$

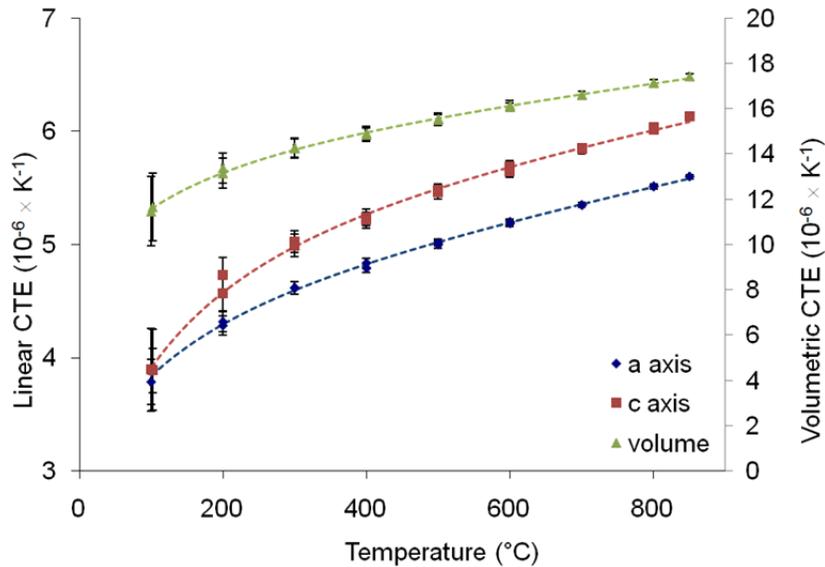
and values are given in Table 1. In this equation,  $\alpha_0$  is the most important term, being similar to the average CTE;  $\alpha_1$  gives the linear dependence on temperature and  $\alpha_2$  describes the curvature. The CTE is least sensitive to  $\alpha_2$  since it's divided by the temperature squared. For each entry, the numbers in the parentheses are the statistical error in the last digit as given by the fitting program.

**Table 1. Coefficients of thermal expansion for B<sub>12</sub>As<sub>2</sub> (25-850°C).**

	$\alpha$ average			
	(10 <sup>-6</sup> K <sup>-1</sup> )	$\alpha_0$ (10 <sup>-6</sup> )	$\alpha_1$ (10 <sup>-9</sup> )	$\alpha_2$
<i>a</i> axis	4.9(6)	4.21(6)	1.30(6)	-0.12(1)
<i>c</i> axis	5.3(7)	4.9(1)	1.2(1)	-0.20(1)
volume	15(2)	13.3(2)	3.9(2)	-0.44(2)

The average coefficients of linear expansion for the *a* and *c* axes were 4.9x10<sup>-6</sup> K<sup>-1</sup>, and 5.3x10<sup>-6</sup> K<sup>-1</sup>, respectively from 25°C to 850°C. There was some anisotropy between the axes, with a 10% difference in the coefficient of thermal expansion for the *a* and *c* axis, which is similar to the 16.2% difference Wu *et al* [16] reported for B<sub>12</sub>As<sub>2</sub> compression in a diamond anvil, and that reported for boron carbide [10-12]. This anisotropy is significant because it shows the fundamental difference in properties that exists in these two different directions in the B<sub>12</sub>As<sub>2</sub> crystal structure.

The large average volumetric thermal expansion coefficient (15.0x10<sup>-6</sup> K<sup>-1</sup>) suggests that in the solution growth of B<sub>12</sub>As<sub>2</sub> crystals, a low cooling rate (<3°C/h) should be adopted. Otherwise, the difference in the coefficient of thermal expansion between the crystals and the nickel solvent (13.4x10<sup>-6</sup> K<sup>-1</sup>) will cause the crystals to be compressed and possibly crack. Additionally, the coefficient of thermal expansion for B<sub>12</sub>As<sub>2</sub> was proposed as one reason for cracking of the heteroepitaxially grown layers [5]. The average coefficients of thermal expansion for Si and 6H-SiC over this same temperature range are  $\alpha_{Si} = 3.8 \times 10^{-6}$  K<sup>-1</sup> and  $\alpha_a = 3.6 \times 10^{-6}$  K<sup>-1</sup>, and  $\alpha_c = 5.1 \times 10^{-6}$  K<sup>-1</sup> respectively [17,18]. These are significantly smaller than values for B<sub>12</sub>As<sub>2</sub>, causing the films to be tensile strained upon cooling from the deposition temperature. If the strain in the film is high enough, it may crack and/or delaminate from the substrate.



**Figure 4 - Linear and volumetric coefficients of thermal expansion of  $B_{12}As_2$  as a function of temperature. Note the large value of the volumetric coefficient (right axis) and the anisotropy of the perpendicular ( $a$  axis) and parallel ( $c$  axis) coefficients (left axis). The dotted lines are fits to the data of the form  $\alpha [K^{-1}] = \alpha_0 + \alpha_1 * T + \alpha_2 / T^2$ , with the values of  $\alpha_0$ ,  $\alpha_1$  and  $\alpha_2$  given in Table 1.**

#### IV. CONCLUSIONS

The coefficients of thermal expansion of icosahedral boron arsenide ( $B_{12}As_2$ ) powder were calculated from HTXRD data taken from room temperature to 850°C. The average coefficients of linear expansion of the  $a$  and  $c$  axes were  $4.9 \times 10^{-6} K^{-1}$ , and  $5.3 \times 10^{-6} K^{-1}$  respectively, ie with a 10% anisotropy in the  $a$  and  $c$  directions. HTXRD revealed a large volumetric coefficient of thermal expansion ( $15.0 \times 10^{-6} K^{-1}$ ), and a 10% anisotropy between the  $a$  and  $c$  directions. Methods of producing high quality  $B_{12}As_2$  bulk crystals and thin films must compensate for the contraction that occurs following synthesis in order to realize strain-free materials.

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